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Structure of CAl_{12}

Ari P. Seitsonen[a)]
Laboratory of Physics, Helsinki University of Technology, 02150 Espoo, Finland

Kari Laasonen
Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104

R. M. Nieminen
Laboratory of Physics, Helsinki University of Technology, 02150 Espoo, Finland

Michael L. Klein
Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104

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The structures of an isolated CAl_{12} cluster and a solid composed of CAl_{12} clusters have been studied using the Car–Parrinello method, based on the density functional theory and the local density approximation. We have compared the results of using the ultrasoft Vanderbilt pseudopotential with those of both a traditional pseudopotential and a linear combination of atomic orbitals method. We have confirmed the high stability of the cluster in its icosahedral structure. However, we show that the cluster-assembled solid is unstable against melting of the clusters, as previously found for $SiAl_{12}$. © *1995 American Institute of Physics.*

I. INTRODUCTION

Interest in clusters and their assemblies has rapidly increased during the last decade. Not only do clusters provide a good testing ground for theories and computational methods, but they can also be used to explore the manner in which solids and alloys are formed from single atoms or molecules. Furthermore, the finite size and large ratio of atoms at the surface vs in the interior gives a unique frame for studying finite-size and surface effects.

An interesting situation occurs when the clusters are positioned into a regularly arranged lattice. If the composition and properties of the cluster is preserved in the lattice a *molecular crystal* has been formed. The everyday example is ice, or in the liquid form water. Moreover, the recent discovery of the third solid form of carbon, the fullerenes,[1] has lead to an enormous number of studies of their properties.

Recently Khanna and Jena[2] proposed that molecular crystals similar to fullerenes, made of cluster constituents, could be prepared by a suitable choice of the atomic and electronic arrangement of the clusters. There would be two main criteria for the composition of the molecular crystals: (i) the intramolecular interaction should be strong, i.e., the isolated cluster must be very stable and (ii) the intermolecular interaction should be weak, i.e., of van der Waals type. To achieve the first requirement Khanna and Jena proposed to use atomic constituents whose total number of valence electrons corresponds to ''magic'' numbers, since such clusters have been found to be very stable.[3] In particular, Khanna and Jena suggested a compact, icosahedral assembly unit with 12 atoms on the outer shell[4] and a single atom at the center of this shell.

The requirements lead Khanna and Jena to the choice of XAl_{12}, X=C,Si,[2,5] where twelve atoms surrounding a central (C,Si) atom are arranged in an icosahedral structure, and the clusters into an fcc crystal. These clusters have 40 valence electrons on closed electronic shells, which is a magic number for jellium clusters.[6,7] Thus, the high icosahedral symmetry is not subject to symmetry-lowering Jahn–Teller distortions. Such clusters were found to have a high dissociation energy.[2,8] Khanna and Jena also argued that CAl_{12} is resistant to reactions with atomic hydrogen.[5]

Here, we report an extension of a previous study of $SiAl_{12}$ (Ref. 9) to CAl_{12} by using *ab initio* molecular dynamics within the density functional theory (DFT), as proposed by Car and Parrinello (Ref. 10). We employ a novel pseudopotential scheme of Vanderbilt[11] to reduce the computational cost. We make comparisons to a conventional pseudopotential and an all-electron calculational method.

Our major results are that the cluster is indeed very stable even at high temperatures, but there is no (local) minimum in the total energy which would be required for the formation of a molecular crystal composed of the CAl_{12} units. We further discuss the general trends of the icosahedral XAl_{12} clusters and possible crystals formed of them.

This paper is organized as follows. Section II briefly introduces the calculational methods. Section III contains the results for the different studies of the isolated CAl_{12} cluster and Sec. IV illustrates the energetics of the proposed cluster-assembled solid. In Sec. V we discuss the results in light of the previous findings for pure aluminium clusters, and in Sec. VI we summarize the main results of this paper.

II. METHODS

For most calculations we have employed the Car–Parrinello (CP) method based on the density functional theory.[10] In our implementation the Kohn–Sham orbitals are expressed with plane waves and only the valence electrons are treated explicitly. The core electrons are replaced by pseudopotentials. For aluminium we use a Bachelet–Hamann–Schlüter (BHS) type pseudopotential[12] with sp nonlocality in the cluster calculations and s nonlocality in the

[a)]Present address: Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6, 14195 Berlin (Dahlem), Germany.

calculations for the solid if not otherwise stated. For carbon we use the ultrasoft pseudopotential (USPP) of Vanderbilt.[11] The use of the ultrasoft pseudopotential is convenient here because a low cutoff can be used and the additional cost due to the overlap operators[13] is negligible because only one atom (four in the case of the solid) is treated with this approach. For details of the implementation of the Vanderbilt pseudopotential scheme one should see Refs. 13 and 14. We find that a cutoff of 15 Rydberg is sufficient to describe the C–Al interaction. For the exchange-correlation terms we use the local density approximation parametrization by Perdew and Zunger.[15]

We also did a few calculations with ordinary norm-conserving pseudopotentials, using the CASTEP code developed by Payne and co-workers.[16] The code employs the optimized Kerker-type pseudopotentials. When applying the code we were mostly limited by the large memory and CPU time requirements due to the large cutoff energy needed. The binding energy of the cluster decreased by ~0.2 eV when going from 40 to 51 Rydberg (see the following), and we were not able to go to higher cutoff energies. The unit cell was smaller than when using the Vanderbilt pseudopotential. We stress that the difference is only due to the efficiency of using the ultrasoft pseudopotential for carbon. The energy of an isolated Al atom is converged to better than 0.1 meV at these cutoff's.

To verify the accuracy of the two pseudopotential methods described, we also calculated the properties of the cluster using an all-electron program DMOL.[17] This method employs a numerical atomic wave function basis set and the whole calculation is done in real space; thus no artificial periodically repeated box was used. The necessary integrals are performed using the discrete variational method.[18] We applied both the local density approximation (LDA) and gradient-corrected (GC) functionals[19] for the description of exchange and correlation.

III. CAl_{12} CLUSTER

Figure 1 shows the ideal geometry of the icosahedral XAl_{12} cluster. Due to the plane wave expansion, one is forced to use periodically repeated images. To decouple the clusters we used a 30 a.u. fcc cell. This cell is found to be sufficient, because at the nearest cluster neighbor distance (21.2 a.u.) the total energy is converged to below 10 meV of the total energy at a cluster distance of 28 a.u. We first confirmed the icosahedral equilibrium structure with the simulated annealing method.[20] The initial condition was a distorted icosahedron at a temperature of ~930 K with the carbon atom at the center of the 12 Al atoms. Two exponential cooling rates were used which brought the temperature to about 1 K in 1.7 and 5.1 ps. The resulting geometry of the both simulations was the icosahedral one with carbon atom at the center.

The effect of the nonlocal Al pseudopotential was investigated by optimizing the structure of the clusters. At the minimum, the C–Al distance was 4.84 a.u. with the *s* nonlocal pseudopotential for Al and 4.69 a.u. with *sp* nonlocality, and the icosahedral symmetry was perfectly preserved. The C–Al distance is somewhat smaller than in the previous works[2,21] and the binding energy is larger. The USPP results are very similar to the values obtained with DMOL and a standard pseudopotential for carbon (see Table I). The short Al–Al distances (compared to bulk Al) are due to the relatively strong and short C–Al bonds that have the tendency to shrink the whole cluster. Overall, our results are in better agreement with the results of Gong and Kumar's[21] than with the original results of Khanna and Jena;[2] the agreement is improved with the corrected results of Khanna and Jena.[8]

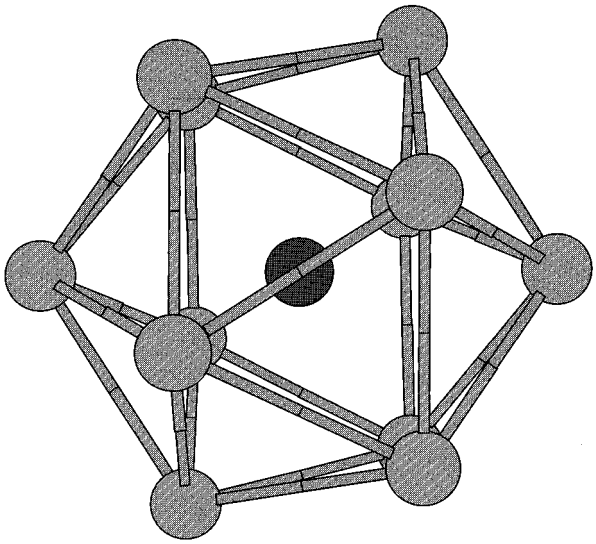

FIG. 1. The geometry of a 13-atom XAl_{12} icosahedron. The coordinates of the Al atoms are $(\pm r_1, \pm r_2, 0)$, $(0, \pm r_1, \pm r_2)$, and $(\pm r_2, 0, \pm r_1)$, where $r_1 = d_{X-Al}[2/(5-\sqrt{5})]^{1/2}$, $r_2 = d_{X-Al}[2/(5+\sqrt{5})]^{1/2}$, and d_{X-Al} is the distance from the central atom to the Al atom on the outer shell, or radius. Thus the ratio between the nearest-neighbor Al–Al distance, d_{Al-Al} and the radius, d_{X-Al}, is $2[2/(5+\sqrt{5})]^{1/2} \approx 1.051$. The Al–Al distances are $2r_2$, $2r_1$, and $2(r_1^2+r_2^2)^{1/2}$. The Al–Al–Al angles are 60° and 108°, the Al–X–Al angles $2 \arctan[(3 \mp \sqrt{5})/2]^{1/2} \approx 63.4°$, 116.6°, and 180°.

We also calculated the structure and binding energy of the XAl_{12} using DMOL with a gradient-corrected exchange-correlation functional.[19] The gradient correction decreases significantly the binding energy and increases the distances

TABLE I. Calculated properties of the CAl_{12} cluster. The bond distances and the binding energy of the cluster are shown. The *s* and *sp* refer to calculations with Vanderbilt pseudo potentials using *s* and *sp* nonlocal components for the aluminum pseudopotential, respectively. GC refers to a calculation using a gradient-corrected exchange-correlation functional.

Method	d(C–Al) (a.u.)	d(Al–Al) (a.u.)	E_{bind} (eV)
CPV (*s*)	4.84	5.09	41.5
CPV (*sp*)	4.69	4.93	45.3
DMOL	4.75	5.00	43.1
DMOL (GC)	4.83	5.08	36.6
CASTEP	4.70	4.95	44.8
Gong and Kumar[a]	5.05	5.31	40.6
Khanna and Jena[b]	5.04	5.30	41.1
Bulk Al[c]		5.41	3.39

[a]Reference 21.
[b]Reference 8.
[c]Experimental values.

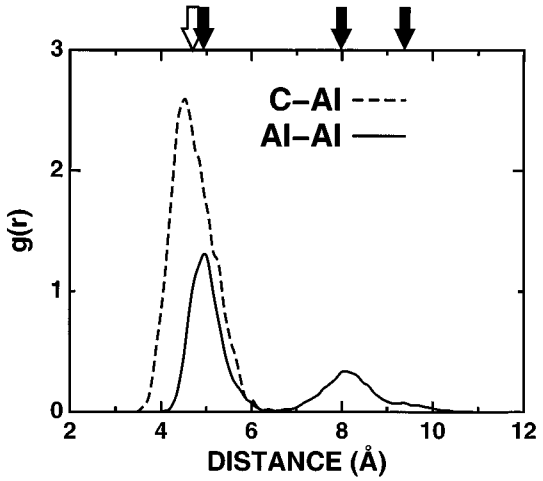

FIG. 2. The pair correlation functions $g(r)$ from the CAl_{12} cluster simulation. The C–Al $g(r)$ is shown with a dashed line and the Al–Al $g(r)$ with a solid line. The Al–Al (C–Al) distances in the ideal, optimized icosahedral structure are shown with solid (open) arrows.

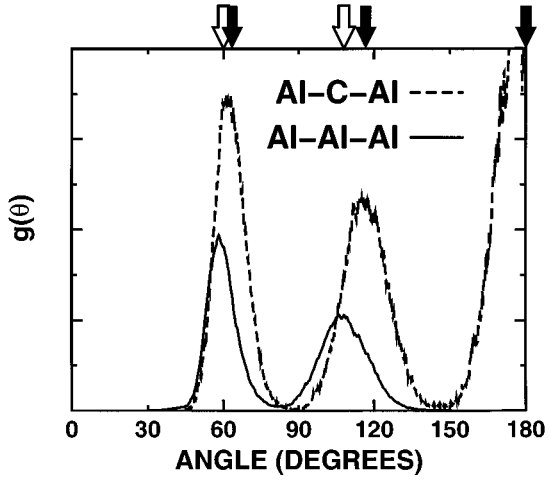

FIG. 3. The angular distributions from the CAl_{12} cluster simulation. The Al–C–Al angles are shown with a dashed line and the Al–Al–Al angles with a solid line. The solid (open) arrows show the Al–Al–Al (Al–C–Al) angles in the ideal icosahedral structure.

between the atoms. Such reduction the overbinding of LDA and increasing the bond lengths are general trends of gradient corrections.

From the point of view of coordination a twelvefold coordinated carbon is very unusual. This unnatural coordination might break the icosahedral symmetry or even result in an unstable cluster. To test the stability of the cluster we performed a molecular dynamics (MD) simulation at a relatively high temperature. The same 30 a.u. fcc cell was used, the time step was 5 a.u. and the effective electronic mass was μ=500 a.u. We started from the cluster of the radius of 4.5 a.u. and with small random displacements to the atomic positions to excite all the vibrational modes. The length of the MD run was 7.7 ps (=64 200 steps). The average temperature of the run was ~930 K.

The main result of the MD run was that the icosahedral structure is stable (up to the melting point of bulk Al=933 K and time of several picoseconds). One could expect that the outer shell of the icosahedron would break into two subshells of 4 and 8 atoms and thus result in a ''natural'' coordination for the carbon. This did not happen and the structure remained closely icosahedral during the whole run. To give some measure of the structure of the cluster we calculated the angular distribution of the nearest-neighbor atoms, the pair correlation functions, and the velocity autocorrelation functions.

The atomic pair correlation function is shown in Fig. 2. The C–Al distance has very large fluctuations, between 3.8 and 6.4 a.u., which is unusual for covalent or metallic bonds. The fluctuation can be compared to the solid, where the C–Al distance is between 3.6 and 4.6 a.u. at a temperature of ~1000 K (see Fig. 6 and Sec. IV). The angular distribution function in Fig. 3 shows a broadening of all the peaks, but the angles are clearly centered around the ideal values.

Due to small inaccuracies on the forces the total angular momentum was not strictly conserved. This caused a very slow rotation of the cluster with a half cycle of about 5 ps. Such low rotation does not effect the results, except for very low frequency vibrations.

The velocity autocorrelation function

$$Z(t)=\frac{\langle \mathbf{v}(t+s)\cdot\mathbf{v}(s)\rangle_s}{\langle \mathbf{v}(s)\cdot\mathbf{v}(s)\rangle_s}, \tag{1}$$

where s denotes the initial states, is shown in Fig. 4. The correlation is not completely vanished during the simulation, which we assign to the small size of the cluster and thus to an incomplete sampling of the whole phase space. The calculated cosine Fourier transform of $Z(t)$,

$$Z(\omega)=\frac{2}{\pi}\int_0^\infty Z(t)\cos(\omega t)dt, \tag{2}$$

is given in Fig. 5. The peak at ~62 THz is close to the vibrational frequency of an Al dimer, 66 THz. Using the harmonic approximation $E(r)=E_0+\frac{1}{2}M\omega^2r^2$ for the radial breathing mode relaxation we obtain a frequency 60 THz. Thus the radial vibration frequency is largely due to the compression of the pairwise Al–Al bonds.

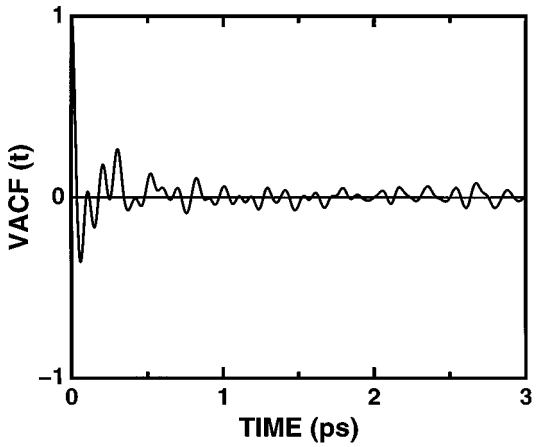

FIG. 4. The velocity autocorrelation function of the CAl_{12} cluster.

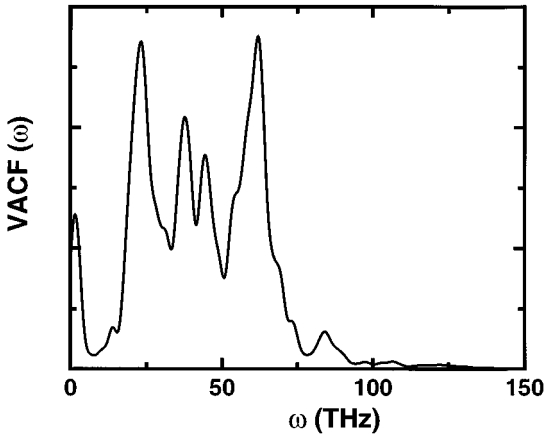

FIG. 5. The Fourier transform of the velocity autocorrelation function of the CAl_{12} cluster.

The carbon centered cluster is stable up to ~1000 K. Although the atomic displacements for the Al atoms become large, the C–Al distance is always larger than 3.7 a.u. Thus the Al atoms remain on single shell around the carbon atom and the carbon does not leave the center.

We also tested if an icosahedral cluster where the carbon is on the surface of the cluster would be stable and if it would have an energy lower than the carbon centered cluster. We performed a MD simulation with a time step of 8 a.u. and fictitious electron mass of 500 a.u. The duration of the run amounted to 1.9 ps (=10 000 steps) and the temperature was 940 K. Within the simulation time the cluster was stable, but the average potential energy was 1.4 eV higher than for the carbon centered cluster. We did not minimize this structure because it clearly is higher in energy than the carbon centered structure.

We observed rapid diffusion of the atoms at the surface of the cluster. This is not unexpected since the temperature is above the melting temperature of Al (933 K). The surface atoms were jumping rather frequently, but the carbon did not jump inside the cluster where it would have a lower energy. Thus the ''diffusion'' on the surface is much faster than the center-to-surface atom exchange. This reflects the very different nature of the center and the surface of the cluster. The overall icosahedral structure was preserved, but was strongly distorted.

IV. CAl_{12} CLUSTER ASSEMBLY

Khanna and Jena speculated that one could construct sophisticated molecular solids (MS) from XAl_{12}-type clusters.[2] Such MS have been produced from fullerenes (C_{60},C_{70}). In fact a very large variety of MS are known, starting from materials as simple as ice (water) to as complicated as crystalline proteins. Common to all these MS is the existence of strong intramolecular bonds and relatively weak intermolecular bonds. This is necessary to preserve the molecular character of the solid, i.e., too strong intermolecular interactions would break the molecules. As an example, one could mention ice at high pressure. At modest pressures ice is formed from water molecules, but at very high pressures when the molecules are pushed close to each other the ''weak'' hydrogen bonds have become as strong as the O–H bonds and a new type of ice is formed where the hydrogen are located between the oxygens.[22] One still has the same chemical composition of ice, but it is no more built of water molecules. Thus it is not sufficient only to have stable clusters to form MS but also the intermolecular interactions have to be small.

TABLE II. Total energy vs lattice parameter for solid CAl_{12} (R_0=4.84 a.u.).

A_{latt} (a.u.)	E_{tot} (a.u.)
20.0	−121.413
21.0	−121.298
21.1	−121.284
21.5	−121.263
22.0	−121.249
23.0	−121.233
24.0	−121.218
30.0	−121.118

A conventional way to view the stability of fullerenes and other clusters forming MS is to consider them as closed shell systems that do not easily change their electronic structure by forming covalent bonds or changing the shape of the molecule. Such systems will still interact via weak bonds. A high one-electron (HOMO-LUMO) gap is characteristic for closed shell systems (~10 eV for water, 20–30 eV for noble gases and ~2 eV for C_{60}). Thus the HOMO-LUMO gap of 2 eV for CAl_{12} obtained with DMOL indicates a fairly strong closed shell character for such a cluster.

The intramolecular interactions are properties of the molecules themselves and thus can be studied with few molecules. In the examples mentioned, the MS are bonded with either hydrogen or van der Waals (vdW) bonds but it is questionable whether aluminium would form such weak, nonmetallic bonds. Very small magnesium and mercury clusters are known to be van der Waals bonded, but in larger clusters the vdW character is replaced with metallic bonding.

The $SiAl_{12}$ clusters turned out not to form a stable cluster phase. Like similar studies presented earlier for $SiAl_{12}$, the molecules break and the resulting structure is basically fcc aluminium with interstitial dopants.[9] Both our calculations and those of and Gong and Kumar[21] give a significantly higher binding energy to the CAl_{12} cluster than to $SiAl_{12}$, making CAl_{12} a better candidate for a MS than $SiAl_{12}$.

To study solid CAl_{12} we chose a cubic unit cell with a varying lattice parameter. The clusters were assumed to form a fcc lattice which is a reasonable assumption for weakly interacting spherical molecules. Thus, we placed four molecules in the simulation cell. Only the Γ-point was used in the simulations. This is equivalent to 4 **k** points in the fcc lattice.

First we calculated the total energies with the fcc lattice parameter A_{latt} varying between 20 and 30 a.u. The radii of the clusters were always set to 4.84 a.u. and one of the symmetry axes of the clusters was chosen in the $(0,[(5-\sqrt{5})/2]^{-1/2}, [(5+\sqrt{5})/2]^{-1/2})$ direction. Only the *s* nonlocality was used for the Al pseudopotential. The total energy vs lattice constant is shown in Table II. The total energy

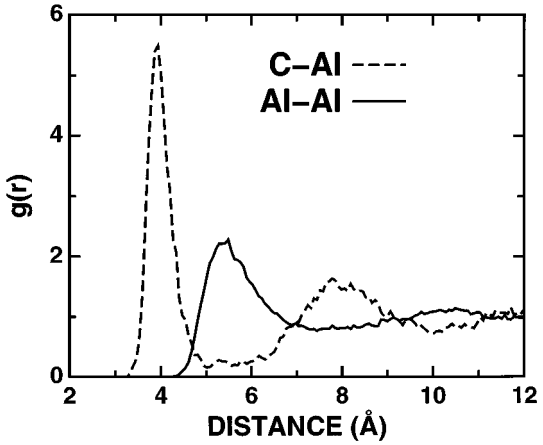

FIG. 6. The pair correlation functions for the CAl_{12} solid taken from the molecular dynamics calculation. The C–Al distances are shown with a dashed line and the Al–Al distances with a solid line.

curve is a strictly monotonically decreasing function in this interval. There is no local minimum which could be interpreted as a MS phase.

To study the dynamical stability of the solid we did a MD simulation using the lattice parameter of 20 a.u. The timestep and the electronic mass were 8.0 a.t.u. and 800 a.u., respectively. To speed up the calculation we used the mass 12 a.m.u. for all the atoms. The length of the run was 1.2 ps (=6000 steps). Our lattice parameter corresponds to a density of 1.90 g/cm^3, which is much lower than the density of bulk aluminium (or carbon). The starting geometry consisted of the ideal clusters of radius of 4.8 a.u., with no initial velocities. The clusters broke up within 0.2 ps and the temperature of the system rose and stabilized to ~1000 K.

The Al–Al and C–Al pair correlation functions are shown in Fig. 6. Both of them are clearly different from those that would arise from the molecular solid phase. The Al–Al pair correlation function is very similar to that for liquid aluminium (see Ref. 23) and the clear first peak of the C–Al pair correlation function has shifted from the 4.8 a.u. of the cluster to 3.9 a.u., while the peak width has reduced from 2.4 to 1.0 a.u. These are dramatic changes and indicate significant changes in the bonding behavior. Indeed, the carbon is now fourfold coordinated. The coordination number is 4.3 ± 0.1, which has been obtained by integrating the C–Al pair correlation function to its first minimum at 5.3 ± 0.2 a.u. From the point of view of the electronic structure of carbon the *fourfold* coordination is of course very natural. The CAl_4 complexes are also very stable. This is reflected by the clear separation of the first C–Al peak from the rest of the pair correlation function and also by simply looking at the atomic configurations. Thus, the final state of this system can be described by carbons (or CAl_4 complexes) *solvated* to liquid aluminium. Clearly, the cluster phase is not stable for the chosen unit cell parameter.

The melting of the cluster phase is not very surprising, because with the 20 a.u. lattice constant the aluminium atoms from the next cluster were only of at the distance of 5.3 a.u., compared with the nearest-neighbor distance in the cluster of 5.1 a.u. To test the further the stability of the cluster phase we studied a somewhat larger cell with the lattice parameter of 22 a.u. corresponding to the density of 1.4 g/cm^3. In this cell the nearest intramolecular Al–Al distance is 6.4 a.u. Here, the atomic positions were minimized starting from the fcc packing of the ideal clusters. After a short minimization the cluster phase again turned out not to be stable. The structure is qualitatively similar to before; the shortest C–Al distance being 3.8 a.u. The coordination of the carbons is again close to four.

V. DISCUSSION

Calculations[24–27] and experiments[28–30] have predicted and confirmed the existence of aluminium clusters. The results show that the icosahedral cluster with 13 atoms is very stable. Furthermore, it is known that Al transition metal (TM) alloys form icosahedral units when rapidly quenched.[31] In modeling these *quasicrystals*,[32] most units used consist of Mackay icosahedra[33] or Al_{12}TM clusters, arranged in a bcc lattice.[34,27] Thus, the latter is equivalent to the structure of a cluster-assembled solid proposed by Khanna and Jena[2] except that (i) the clusters would be in a bcc arrangement, not fcc, and (ii) the carbon atom at the center of the icosahedron is replaced with a transition metal atom (see the following for a discussion of the relative stability of XAl_{12} clusters). Transition metal clusters often form icosahedral structures.

Our results show that the total energy curve of the cluster-assembled solid is monotonically decreasing to from $A_{\mathrm{latt}}=30$ to 20 a.u. and that the cluster phase breaks down already at $A_{\mathrm{latt}}=22$ a.u., giving strong evidence that the cluster phase is not stable. We do not find any sign of the a weakly interacting van der Waals region in our calculations (e.g., a shallow local minimum for large lattice parameters). One should keep in mind that our calculations are based on LDA, which has a tendency to exaggerate weak bonds like hydrogen or van der Waals bonds. Because the breaking mechanism of the clusters is the forming of intramolecular Al–Al bonds, we believe that LDA is capable to describe this correctly. Even if there would be computationally a MS phase with $A_{\mathrm{latt}}>21$ a.u. the density of that phase would be unrealistically low and thermal fluctuations would destroy the MS phase. In any case, calculated results should always be checked with respect to the exchange-correlation functional if a weak bonding is to be expected.

Why does the apparently closed-shell CAl_{12} molecule not form a molecular solid? The electron density is not as well localized as in materials such as carbon (fullerenes) and water, thus requiring a relatively large Al–Al distance to avoid strong intermolecular interactions. Moreover, the cluster has built-in instabilities due to the unnatural bonding environment for the carbon atom. The stability of a single cluster is due to the aluminium atoms. They prefer a high coordination and spherical shape, but this structure is not very stable towards external perturbations. The carbon would like to break the 12 atom outer shell to two shells of 4 and 8 atoms. We see clear evidence for this in the solid phase.

The isolated cluster is very stable, but the observed very large fluctuations on the C–Al distance, 2.4 a.u. or 50% from the average bond length, are not in agreement with the concept of strong covalent or metallic bond. The picture that

arises is more that the carbon atom is *not* bonded to any fixed aluminium atoms and can ''rattle'' around the centre of the cage. The maximum displacement ($|\mathbf{R}(t)-\mathbf{R}(0)|$) of the carbon is 0.85 a.u., which broadens the C–Al peak up to 1.7 a.u. The average displacement is only 0.35. This means that the movement of the carbon atom is restricted by the cage formed by the aluminium atoms and the space where it can reside is very limited.

In the case of the solid one clearly sees the change of the coordination number of carbon from 12 to 4. The bonding between the carbon and aluminium in the final structure is a normal covalent bond. The coordination number is typical for carbon, the bond distance reasonable and the fluctuations in the distance are small ($\sim$1 a.u.). Thus the breaking tendency is stronger than the closed shell stabilization, at least up to a fcc lattice parameter A_{latt} of 22 a.u.

We also studied the general stability of neutral XAl_{12} clusters, X going through from H to Xe.[21,35] The calculations were done with DMOL and forcing the icosahedral symmetry. We found that the highest binding energies were, in descending order, for X=C, Ru, Rh, B, Ni, O, Si, Co, and N. Least bound are, naturally, the clusters containing a rare gas atom at the center. The usage of gradient corrections does not change the order in binding energies significantly but rather causes a reduction of about 5 eV. Note that for singly negative XAl_{12}^- an enhanced stability has been found, e.g., in the case of Al_{13}^- and BAl_{12}^-.[29,30] The high stability of the group III Al_{12}^- is again a consequence of the magic number, 40, of valence electrons. However, we have not studied the charged clusters in the present work.

Recently, Khanna and Jena[36] further suggested a new cluster-assembled crystal phase, which would consist of Al_{13} clusters and potassium (or more generally, alkali metals) atoms, arranged to a CsCl lattice. The lattice would be stabilized as the K atom would partially donate its lone, loosely bound valence electron to the Al_{13} cluster. Thus the cluster would be negatively charged and would carry the magic number, 40, of valence electrons. This ionic solid can be stable since the long-range Coulomb interaction is screened by the alternating positive and negative charge. The $K^+Al_{13}^-$ solid resembles the pseudobinary, intermetallic alloy $La(Fe_xAl_{1-x})_{13}$ (Refs. 37 and 38), which has been suggested to consist of mixed 13-atom Fe–Al icosahedral clusters and has been found to form a stable cluster solid.[38] However, to our knowledge only solids with $0.46 \leqslant x \leqslant 0.92$ have been reported.

VI. CONCLUSIONS

We have observed an unusual bonding behavior between the carbon and aluminium in the CAl_{12} cluster. Our simulations show the large stability of the cluster, but does not give any support for the formation of a cluster assembled crystal.

It does not seem very likely that XAl_{12} molecular solids can be formed, at least when X is a group IV atom. Of these clusters the one having carbon inside should have the highest binding energy, but also the strongest tendency to break the outer shell and form fourfold coordinated complexes. Silicon should have the same but less pronounced behavior and from an earlier simulations the cluster phase is known to be similarly unstable.[9] Going down column IV the tendency to form *fourfold* coordinated structures diminishes, but so will the binding energy.

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